

# PATENT SPECIFICATION

(11) 1 528 932

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- (21) Application No. 38818/75 (22) Filed 22 Sept. 1975  
 (31) Convention Application No. 7 432 960  
 (32) Filed 27 Sept. 1974 in  
 (33) France (FR)  
 (44) Complete Specification published 18 Oct. 1978  
 (51) INT CL<sup>1</sup> C08C 19/06//B32B 27/04, 27/08  
 (52) Index at acceptance  
     C3P D9A1X D9A3 D9A7 D9A8 D9B16 D9D2 D9E2  
     B5L B2  
     B5N 0712 1504 1518 2706 2728  
     C3M 127C 130 134 D



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## (54) POLYBUTADIENE DERIVATIVES, THEIR PREPARATION AND USE

(71) We, INSTITUT FRANCAIS DU PETROLE, a body corporate organised and existing under the laws of France, of 4, avenue de Bois-Preau, 92502 Rueil-Malmaison, France, and INSTITUT FRANCAIS DU OAOUTCCHOU, a body corporate organised and existing under the laws of France, of 42, rue Scheffer, 75016 Paris, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the preparation of modified polymers derived from amorphous 1—2 polybutadienes, to the modified polymers so prepared, and their use. It particularly concerns the epoxidation, by means of perphthalic acid, of amorphous 1—2 polybutadienes (PB 1—2) in solution. It also concerns further derivatives of the epoxidized amorphous 1—2 polybutadienes so prepared and their applications.

The polymers used in this invention have a molecular weight higher than 20,000; they contain at least 50% of 1—2 addition units (preferably 70 to 96% of 1,2 units) and have a crystallinity, at 20°C, lower than 5%.

These properties of the polymers may be determined as follows:

the molecular weight by viscosimetry on a toluenic solution at 30°C,  
 the microstructure (content of 1,2 units) by infra-red spectrometry, according to the method described by Ciampelli et al in "La Chimica e l'Industria" 41, 1959, page 758,

the crystallinity at 20°C, by X-ray diffraction and by fractionation in ethyl ether according, for example, to the method described in the Belgian patent 549,554 or in the French patent 1,154,938.

Accordingly, there is provided by the invention a process for preparing epoxidized 1,2-polybutadiene, which comprises reacting a solution of amorphous 1,2-polybutadiene having a viscosimetric molecular weight higher than 20,000, containing at least 50% of 1,2-added units and having a crystallinity at 20°C lower than 5%, with a mono-perphthalic acid solution in an amount sufficient to obtain the desired degree of epoxidation, removing the phthalic acid formed during the reaction and separating the epoxidized 1,2-polybutadiene so obtained.

The epoxidation of homopolymers and copolymers of butadiene has been the object of numerous studies which are summarized in the book "Chemical Reactions of Polymers" High Polymers — Volume XIX, E. M. Fettes, Interscience Publishers, New York, 1964, p. 152—172. As a general rule, it is considered (W. Dittmann and K. Hamann in Chemiker-Zeitung 95 Jahrgang (1971) n° 15/16, p. 684—692) that polybutadienes having a predominant 1—4 structure are more easily epoxidized than those having a 1—2 structure.

However, in order to illustrate the state of the art, we will mention certain patents indicating some compositions based on polybutadienes, preferably 1—2, epoxidized, but these polybutadienes are of low molecular weight and consequently lead to the formation of products which cannot be directly used as elastomers. These patents are, for example U.S. P 3,073,792 and 3,742,086 and the Japanese published patent applications 73—43186 and 73—34372.

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These patents not only contemplate a field of application limited to the polybutadienes of low molecular weight but, in addition, they generally make use, as epoxidation reactants, of aliphatic peracids (performic or peracetic acid) added separately or formed in situ in the reaction medium. These compounds have the disadvantage of liberating, in the modified polybutadiene solution, strong acids (formic or acetic acid), which produce numerous secondary reactions in which a large amount of the formed epoxy groups is consumed to give partially cross-linked products i.e. products insoluble in the organic solvents, which makes it very difficult to use such materials.

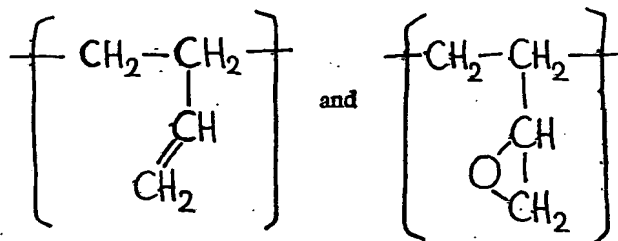
U.K. Specification No. 837,689 discloses the possibility of using a number of peracids, including monoperphthalic acid, in the epoxidation of 1,2-poly(diolefins), but does not relate to treatment of the amorphous polymer with which this specification is concerned.

The epoxidation process of the invention makes use of monoperphthalic acid which is converted to phthalic acid insoluble in the solutions of amorphous PB 1,2. Due to this insolubility it is possible to separate and recover easily said acid, thereby preventing any liability of opening or polymerization of the oxirane rings as generally observed when using other peracids.

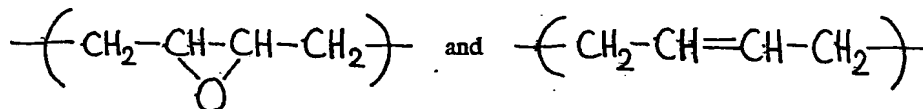
This epoxidation in homogeneous phase is considerably facilitated by the very good solubility of the starting amorphous 1—2 polybutadienes in the usual organic solvents.

The present invention therefore concerns the epoxidation of amorphous polybutadienes containing at least 50% of 1—2 units and having a molecular weight preferably from  $10^5$  to  $2.10^6$ , in the presence of monoperphthalic acid.

Depending on the rate of modification  $n$ , as hereinafter defined (see Example 1 below), there is obtained, by this process, epoxidized polybutadienes containing units of the formulae:



these units constituting at least 50% of the recurring units forming the polymer chain, the other recurring units being essentially epoxidized or non-epoxidized 1—4 units, of the formulae:



The epoxidation process of the invention is very simple and has a wide field of applicability since it makes it possible to vary the epoxidation rate of 1,2 polybutadiene from a few percents, e.g. 3%, to 80% or more, so as to obtain, from the same starting product, a large variety of materials having particular properties and including both the elastomers and resin fields.

The rate of modification (and consequently the physico-chemical and technical properties of the modified products) may be selected at will by adjusting the amount of peracid in contact with the polymer. According to a preferred embodiment of the invention, we use, as basic material, solutions of 1—2 PB, such as produced by the polymerization reaction described, for example, in U.S. P 3,772,263, without any preliminary purification step.

The epoxidation reaction being conducted at temperatures close to room temperature and without any pressure increase, it is possible to proceed in a very conventional plant of the same type as that used for polymerization.

As compared to the unmodified products, the epoxidized 1,2 polybutadienes, as obtained, have numerous advantageous properties:

- better sticking to textile fibers and to various materials (e.g. metals, glass, wood),
- improved compatibility with certain polar resins (epoxy, phenoplastic, amino-plastic resins),
- stabilization effect and improvement of certain properties of elastomers and resins (rubbers derived from polychloroprene, butadiene-acrylonitrile copolymers, poly vinyl chloride),
- improvement in the modulus and breaking strength (among other mechanical properties) as pure gum mixtures or with fillers,
- access to new chemical reactions particularly by crosslinking of the epoxide groups, opening thereof and grafting of various chemical radicals on the oxirane rings,
- improvement of the resistance to solvents of the hydrocarbon type, mainly gasolines, and to the various ageing factors.

The epoxidation process of the invention can suitably be conducted at temperatures from  $-25$  to  $+80^{\circ}\text{C}$  and preferably from  $0$  to  $+50^{\circ}\text{C}$ . We preferably use solvents or mixtures of solvents already employed for the preparation of amorphous 1—2 polybutadiene, e.g., aromatic, aliphatic, cycloaliphatic hydrocarbons or their mixtures with esters such as alkyl acetates. Perphthalic acid is, for example, dissolved in an ester and/or in an ether. After the reaction has been completed, the formed solid phthalic acid is recovered by filtration or centrifugation; the modified polymer may be subsequently separated from the filtrate, either by evaporation or steam-stripping of the solvent, or by precipitation or coagulation of the polymer in the presence of a non-solvent which may be, depending on the rate of epoxidation of the polymer, either an alcohol such as methyl, ethyl or isopropyl alcohol, or a light hydrocarbon, such as pentane or gasoline. Finally the polymer is dried under reduced pressure or in a ventilated oven up to a constant weight.

In view of their properties, the epoxidized amorphous 1—2 polybutadienes obtained by the process of the invention may have a large number of useful applications:

They can be used as raw material for manufacturing amine adducts suitable for use as rubber additives, by their reaction with amines under conditions such that at least a proportion of the epoxy (oxirane) groups condense with molecules of the amines, for example in the presence of a catalyst for the condensation, and in solution in a hydrocarbon solvent. (See for example Example 12 below).

They can also be used as raw material for manufacturing membranes of selective permeability. Their reaction with formic acid followed by saponification yields hydroxypolybutadienes. Cross-linking agents give cross-linked reaction products of these latter derivatives which swell in water and are hence useful for making selectively permeable membranes.

They can also be used as components of rubber compositions vulcanizable by means of sulfur, and can thus be used to make vulcanizable elastomer compositions in admixture with conventional vulcanization ingredients, e.g. sulfur. Such compositions can be compositions comprising polar elastomers, e.g. butadiene-nitrile acrylic copolymers, or polychloroprenes. (See for example Examples 14—16). Such use of the epoxidized polybutadienes in polar rubber compositions such as those comprising polychloroprenes and nitrile rubbers can give improved mechanical properties and resistance to ageing in the vulcanized compositions obtained.

They can still further be used in adhesive compositions, for example for bonding metals, wood or leather: optionally in preparing such compositions the polybutadiene can have been degraded partially before use by treatment with a depolymerizing agent: see for example Example 17 (b). Such adhesive compositions can suitably comprise the epoxidized polymers in solution in a hydrocarbon-containing solvent in the presence of a hardening agent.

The following non-limitative examples illustrate particular embodiments of the invention while giving further experimental details.

In the examples describing the manufacture, by the process of the invention, of epoxidized amorphous 1—2 polybutadienes, the starting materials used are solutions (at concentrations from 30/50 g/liter) of amorphous 1—2 polybutadiene prepared according to the process described in U.S. Patent Specification No. 3,772,263 by using a mixture of toluene and ethyl acetate (95 and 5% by volume respectively) as solvent.

The viscosimetric molecular weight of the polymer so produced is close to 1.8.

10<sup>6</sup> and its microstructure, as determined by infra-red spectrum, using the extinction coefficient in accordance with Ciampelli et al (*La Chimica e l'Industria*, 41, 758 (1959)) for the band at 910 cm<sup>-1</sup>, corresponds to 95—96% of 1—2 bonds and does not include detectable isotactic or syndiotactic structures, the crystallinity being lower than 2%.

The total unsaturation is determined by catalytic hydrogenation in the presence of PdCl<sub>2</sub>, deposited on CaCO<sub>3</sub>, (*Revue Générale du Caoutchouc*, 45, 739 (1968)): it corresponds to 95—96% of unsaturated units.

The gel rubber content is lower than 1% by weight; the proportion of oxygen combined with the polymer (determined by microanalysis) is 0.6% by weight.

#### EXAMPLE 1.

We dissolve 2 kg of monoperphthalic acid in 11 l. of ethyl acetate and we filter on fritted glass to remove the inorganic salts from the product. The iodometric determination of the amount of perphthalic acid present in the solution indicates a peracid content of 0.7 mole/liter (127.4 g/l). This solution is stored in a refrigerator.

Into a flask provided with a stirrer and a nitrogen inlet, we introduce 4 liters of a solution (toluene-ethyl acetate) of 1—2 PB at a polymer concentration of 33 g/l (i.e. 132 g) and we add subsequently 2 liters of toluene for decreasing the viscosity of the medium. After removal of atmospheric oxygen by bubbling into the medium a gentle nitrogen stream, we introduce, by means of a bromine funnel, 520 cc of a solution of perphthalic acid in ethyl acetate (i.e. 66.3 g of peracid). The reaction is continued for 10 hours at room temperature under nitrogen atmosphere and with stirring. The solution is filtered and then added to 10 liters of ethyl alcohol. A white product precipitates. It is dried in a ventilated oven at 25°C. Its analysis shows the respective contents:

$$C\% = 84.94 \quad H\% = 10.64 \quad O\% = 4.35$$

Under IR, the presence of epoxy rings is confirmed by specific bands at 750—870 and 1.240 cm<sup>-1</sup> accompanied with a decrease of the unsaturation peak at 910 cm<sup>-1</sup>. By magnetic nuclear resonance (MNR) there is observed a band at 2.70 ppm attributable to a tertiary hydrogen on an epoxy ring. The specific determination of the epoxy groups is carried out by reacting the latter with nascent HBr formed by reaction of perchloric acid with triethyl ammonium bromide (in a chloroform- ketone- or ester-containing medium depending on the rate of modification). This determination shows that more than 95% of the introduced oxygen is in the form of epoxy groups.

From the determination of the oxygen content it is possible to calculate the modification rate  $n$  which is the number of modified "butadiene" monomer units in a chain fraction of 100 recurring units. The value of  $n$  is given by the formula:

$$n = \frac{54 \times a}{16 (100 - a)} \times 100$$

in which:

$a$  is the oxygen content of the modified polymer from which is deduced the amount of oxygen combined to the starting 1—2 PB.

In the present example we have:

$a = 4.3 - 0.6 = 3.7$ , accordingly

$$n = \frac{54 \times 3.7}{16 \times 96.3} \times 100 = 13$$

The reaction yield with respect to the amount of peracid introduced is 88%.

#### EXAMPLES 2 to 5.

We proceed in the same manner as above described except that the amount of peracid introduced in to the medium is varied.

Example No.	Perphthalic acid (g)	1-2 PB (g)	Modification rate expressed as the number of oxirane groups %
2	17.5	192(1)	3
3	134	132	29.7
4	311	132	55
5	356	132	60

(1)— In this example, the solution of amorphous 1-2 PB is at a concentration of 48 g/liter.

For a modification rate higher than 30, the modified polymer is precipitated by using gasoline or a hydrocarbon of the pentane type as non-solvent, after removal of the formed phthalic acid, by filtration or centrifugation.

#### EXAMPLE 6.

We proceed in the same manner as in example 1 and with the same amounts of reactants but the reaction is stopped after 4 hours of contact of the reactants. The content of oxygen combined to the modified product is 2.9% (i.e.  $a=2.3\%$ ) which corresponds to a modification rate of  $n=7$ . The modification rate can thus be varied by changing the reaction time, this being a confirmation of the large capacity of adjustment of the epoxidation process since the reaction time as well as the amount of peracid introduced both regulate the final modification rate.

#### EXAMPLES 7 to 11.

In the same operating conditions as in example 1, we have prepared amorphous 1-2 polybutadienes having the following modification rates:

Example No.	Modification rate expressed as the number of oxirane groups %
7	10
8	15
9	16
10	25
11	50

#### EXAMPLE 12.

We use a toluene solution of epoxidized 1,2 polybutadiene corresponding to example 4, the polymer concentration being adjusted to 13.5 g per 1,750 cc of toluene. This solution is reacted, by heating at  $100^{\circ}\text{C}$  for 11 hours, with 61.8 g of 4 amino N,N diethylaniline, in the presence of 10 g of phenol used as catalyst for fixing the amine on the oxirane groups. The reaction product is soluble in ethyl alcohol and in acetone and it precipitates by addition of pentane, this feature making possible its purification. Its analysis gives:

$$O\% = 12.26 \quad N\% = 2.24$$

After drying this product appears in the form of a brown powder, dispersable in rubber mixtures, non-extractable from the latter by aqueous media or by volatilization resulting from the heat effect. The secondary amino groups thus combined with the epoxidized polybutadienes, improve the resistance to heat of the elastomer mixtures.

**EXAMPLE 13.**

10 g of epoxidized polybutadiene corresponding to example 3, is dissolved into 150 cc of toluene. We further add thereto 40 g of pure formic acid in solution in 30 cc of distilled water. The mixture is vigorously stirred for 24 hours at room temperature. After decantation the aqueous layer is removed. The polymer is then saponified by stirring at ordinary temperature for 12 hours with a solution of 16 g of soda in an alcohol-water mixture.

After purification and drying, the proportion of combined oxygen (11.68%) corresponds to the opening of the major part of the oxirane groups in the form of glycols.

The formed hydroxy polybutadiene swells in water after cross-linking, and we can take advantage of this property by using the hydroxypolybutadiene so crosslinked for manufacturing thin membranes of selective permeability. In addition, the possibility of opening certain epoxy groups is favorable to the obtainment of adhesives for metals, the formed OH groups being considered as responsible for the adhesive properties in the case of the epoxy resins.

**EXAMPLE 14.**

We vulcanize at 143°C for 30 minutes a sample of conventional 1,2 polybutadiene and a sample of epoxidized 1—2 polybutadiene (n=10) prepared according to example 7. The vulcanization system is conventional in the rubber industry:

— Polymer	100	parts b. w.
— stearic acid	2	" "
— zinc oxide	3	" "
— cyclohexylbenzothiazylsulfenamide	0.8	" "
— sulfur	2.0	" "

As compared to the unmodified 1,2 PB, the epoxidized derivative exhibits improved properties concerning hardness, modulus, tear strength and a lower sensitivity to solvents of the type of aromatic hydrocarbons or gasoline.

	Conventional 1,2 PB		Epoxidized 1,2 PB (1)	
	without filler	with filler (2)	without filler	with filler (2)
—Breaking strength (DaN/cm <sup>2</sup> )	10	104	29	130
—Lengthening at break (%)	540	440	480	350
—Modulus 200% (DaN/cm <sup>2</sup> )	—	54	—	60
—Hardness (° share)	40	70	48	74
—Swelling in chloroform (%) (3)	400	280	320	220
—Swelling in toluene (%) (3)	400	250	300	205
—Swelling in acetate (%) (3)	180	120	210	135
—Swelling in gasoline (%) (3)	290	170	220	130

(1)—modification rate n=10

(2)—50 p, of silica b. w.

(3)—maximum swelling (%) by volume) after immersion for 48 hours at 23°C.

Due to its particular structure with the unsaturation located outside the main chain, the 1,2 polybutadiene exhibits excellent properties of resistance to ageing, which are not altered by the epoxidation reaction.

	Conventional 1,2 PB		Epoxidized 1,2 PB (1)	
	without filler	with filler (2)	without filler	with filler (1)
-Breaking strength (%) (3)	-10	+25	+15	+40
-Tear strength (%) (3)	-	+9	-	+4
-Hardness shore (%) (3)	+1	0	0	+1

(1)-modification rate  $n=10$

(2)-50 p. of silica b. w.

(3)-variations of the properties expressed in % after ageing in a ventilated oven for 7 days at 100°C.

#### EXAMPLE 15.

Epoxidized polybutadienes are compatible with polar rubbers such as butadiene-nitrile acrylic copolymers and polychloroprenes, thus imparting to the latter improved mechanical properties and resistance to ageing.

By way of example a mixture of 90 parts b. w. of polychloroprene and 10 parts b.w. of epoxidized 1—2 polybutadiene vulcanizes at 143°C in the presence of sulfur as vulcanization agent.

With the use of epoxidized amorphous 1—2 polybutadienes prepared according to examples 2 to 9, we have obtained vulcanizates having the following properties:

— Polychloroprene 90 p. + 1—2 PB ( $n=3$ ) 10 p :

— Breaking strength : 190 DaN/cm<sup>2</sup>

— Hardness : 42° Shore

— Polychloroprene 90 p. + 1—2 PB ( $n=16$ ) 10 p :

— Breaking strength : 100 DaN/cm<sup>2</sup>

— Lengthening at break : 800%

— Hardness : 42° Shore.

#### EXAMPLE 16.

We admix 330 g of 10% epoxidized 1—2 PB of example 7 with 45 g of meta-phenylenediamine. By heating in a pressing-machine at 143°C for 40 minutes, we obtain a vulcanized product having, in a mixture without filler, a lengthening at break of about 500%.

#### EXAMPLE 17.

(a) We use 50% epoxidized 1—2 polybutadiene of example 11. Two blades of ordinary steel (30 microns thick), previously degreased with trichloroethylene, are coated with a solution of said epoxidized polybutadiene (polymer concentration : 100 g/l, solvent : toluene-ethyl-acetate) containing 10% of m. phenylenediamine (b. w. with respect to the rubber). The two plates are assembled under a pressure of 3—4 kg/cm<sup>2</sup> and then heated for 2 hours at 80°C. The pressure is released and heating is continued for 4 hours at 140°C. The measurement of the tensile strength (80 DaN/m<sup>2</sup>) and of the peeling strength, indicate good adhesive properties of the mixture. In addition the resistance of the adhesive to boiling water is satisfactory. The epoxidized polybutadienes also exhibit good adhesive properties for wood and leather.

(b) In order to improve these adhesive properties further it can be desirable to increase the polymer concentration of the adhesive solution. This can be achieved in an alternative embodiment by a preliminary partial degradation of 1—2 PB in the polymerization solvent, e.g. by adding 5% b.w. of dioxylmercaptan to the solution and heating for 10 hours at 135°C: otherwise this embodiment is carried out similarly to the foregoing part (a) of this Example.

We thus obtain concentrations of 1—2 PB amounting to 250—300 g/l and a sufficiently fluid medium for proceeding to the epoxidation and to the direct use of the solution of modified polymer as an adhesive agent.

## EXAMPLE 18.

Example 17 is repeated with two blades of ordinary annealed steel of 0.1 mm thickness, previously degreased by means of trichloroethylene and pretreated with a phosphating agent.

We made use of the epoxidized amorphous 1—2 polybutadienes of example 8 (n=15) and of example 10 (n=25).

The hardening agent was diethylenetriamine. Test of resistance to unsticking by shearing (dynamometer Lhomargy — traction speed : 10 cm/min), gave the following results:

- |    |   |    |
|----|---|----|
| 10 | — epoxidized 1—2 PB (n=15) : 25 DaN/cm <sup>2</sup> | 10 |
|    | — epoxidized 1—2 PB (n=25) : 38 DaN/cm <sup>2</sup> |    |

## EXAMPLE 19.

We stick together two plates of plywood (4 mm thick, covering surface of 400 mm<sup>2</sup>) with a solution of epoxidized polybutadiene (n=25) of example 10 in toluene, the hardening agent being diethylene tetramine. The bonded plates are pressed for one hour at room temperature and then brought to 100°C for 8 hours.

Resistance of the bond to rupture by shearing is then 15 DaN/cm<sup>2</sup>.

## WHAT WE CLAIM IS:—

- |    |   |    |
|----|---|----|
| 20 | 1. A process for preparing epoxidized 1,2-polybutadiene, which comprises reacting a solution of amorphous 1,2-polybutadiene having a viscosimetric molecular weight higher than 20,000, containing at least 50% of 1,2-added units and having a crystallinity at 20°C lower than 5%, with a monoperphthalic acid solution in an amount sufficient to obtain the desired degree of epoxidation, removing the phthalic acid formed during the reaction and separating the epoxidized 1,2-polybutadiene so obtained. | 20 |
| 25 | 2. A process according to claim 1, in which the starting amorphous 1,2-polybutadiene has a viscosimetric molecular weight of from 100,000 to 2,000,000 and contains from 70 to 96% of 1,2-added units.  | 25 |
| 30 | 3. A process according to claim 1 or 2, in which the amorphous 1,2-polybutadiene starting material is reacted in solution in a hydrocarbon solvent or in a mixture of a hydrocarbon solvent with an ester solvent.  | 30 |
|    | 4. A process according to any one of claims 1 to 3 in which the monoperphthalic acid is used in solution in an ester solvent or in an ether solvent.  |    |
| 35 | 5. A process according to any one of claims 1 to 4, in which the epoxidation reaction is conducted at a temperature in the range -25°C to +80°C.  | 35 |
|    | 6. A process according to claim 1, substantially as hereinbefore described with reference to any one of Examples 1—11.  |    |
|    | 7. Epoxidized 1,2-polybutadiene prepared by a process according to any one of claims 1 to 6.  |    |
| 40 | 8. A process for preparing an amine adduct of epoxidized 1,2-polybutadiene, which comprises reacting epoxidized 1,2-polybutadiene according to claim 7 with an amine under conditions such that at least a portion of the epoxy groups condense with molecules of the amine.  | 40 |
| 45 | 9. A process according to claim 8, wherein the epoxidized 1,2-polybutadiene is reacted in solution in a hydrocarbon solvent in the presence of a catalyst capable of catalysing the condensation.   | 45 |
|    | 10. A process according to claim 8, substantially as hereinbefore described with reference to Example 12.   |    |
| 50 | 11. An additive for an elastomer composition, comprising an amine adduct of epoxidized 1,2-polybutadiene prepared by a process according to claim 8, 9 or 10.   | 50 |
|    | 12. An elastomer composition comprising an additive according to claim 11.  |    |
|    | 13. A process for preparing a hydroxypolybutadiene which comprises reacting epoxidized 1,2-polybutadiene according to claim 7 with formic acid, and thereafter saponifying the polymeric product so obtained.   |    |
| 55 | 14. A process according to claim 13, substantially as hereinbefore described with reference to Example 13.  | 55 |
|    | 15. A hydroxypolybutadiene prepared by a process according to claim 13 or 14.   |    |
|    | 16. A selectively permeable membrane comprising a cross-linked reaction product of a hydroxypolybutadiene according to claim 15 with a cross-linking agent.   |    |
| 60 | 17. An adhesive composition comprising an epoxidized 1,2-polybutadiene according to claim 7.  | 60 |
|    | 18. A composition according to claim 17, comprising the epoxidized 1,2-poly-  |    |



butadiene in solution in a hydrocarbon-containing solvent in the presence of a hardening agent.

19. A composition according to claim 17, substantially as hereinbefore described with reference to Example 17(a), 18, or 19.

20. A composition as defined in claim 17 or 18, wherein the polybutadiene has been partially degraded by treatment with a depolymerising agent.

21. A composition according to claim 20, substantially as hereinbefore described with reference to Example 17(b).

22. A vulcanizable elastomer composition comprising an epoxidized 1,2-polybutadiene according to claim 7 in admixture with conventional vulcanization ingredients.

23. A composition according to claim 22, wherein the vulcanization ingredients comprise sulfur.

24. A composition according to claim 22 or 23, which comprises a polar elastomer.

25. A composition according to claim 24 wherein the polar elastomer is a butadiene-nitrile acrylic copolymer, or a polychloroprene.

26. A composition according to claim 22, substantially as hereinbefore described with reference to any one of Examples 14, 15, and 16.

27. A vulcanized elastomer composition obtained by heating a composition according to any one of claims 22—26 under vulcanization conditions.

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